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Photocleavage Reactions of Monothioimides

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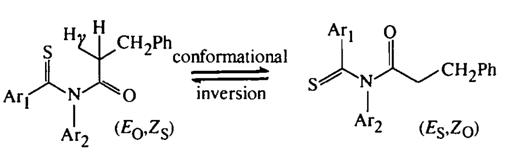
Abstract

The photochemistry and crystal structures of four monothioimides have been studied: *N*-phenyl-3-phenyl-*N*-[phenyl(thiocarbonyl)]propanamide, $C_{22}H_{19}NOS$, (1*a*); *N*-(4-bromophenyl)-*N*-[phenyl(thiocarbonyl)]-3-phenylpropanamide, $C_{22}H_{18}BrNOS$, (1*b*); *N*-(4-bromo-2,6-dimethylphenyl)-3-phenyl-*N*-[phenyl(thiocarbonyl)]-propanamide, $C_{24}H_{22}BrNOS$, (1*c*); and *N*-[4-methoxyphenyl(thiocarbonyl)]-*N*-phenyl-3-phenylpropanamide, $C_{23}H_{21}NO_2S$, (1*d*). All four molecules adopt similar (E_S,Z_O) conformations, which are not suitable for photochemical γ-hydrogen abstraction; short intramolecular O···C(S) contacts (2.8 Å) suggest a new mechanism with nucleophilic attack by the carbonyl O atom on the C═S double bond; the presence of water is also essential for the reaction to proceed.

Comment

Acyclic monothioimides of general structure (1) [see scheme below, which shows two conformations of the monothioimides; others are (*Z,Z*) and (*E,E*)] undergo photochemical reactions when irradiated in solution to give, among other products, thiobenzanilides, (2) (Sakamoto *et al.*, 1991). The reasonable mechanism suggested for this reaction involves Norrish type II γ-hydrogen abstraction by sulfur (see scheme), followed by 1,4-biradical cleavage.



(observed crystal conformation)

	Ar_1	Ar_2
(1*a*)	Ph	Ph
(1*b*)	Ph	$4\text{-}BrC_6H_4$
(1*c*)	Ph	$4\text{-}Br\text{-}2,6\text{-}diMeC_6H_2$
(1*d*)	$4\text{-}MeOC_6H_4$	Ph

$$\downarrow h\nu$$

Ar_1—CS—NH—Ar_2 (2)

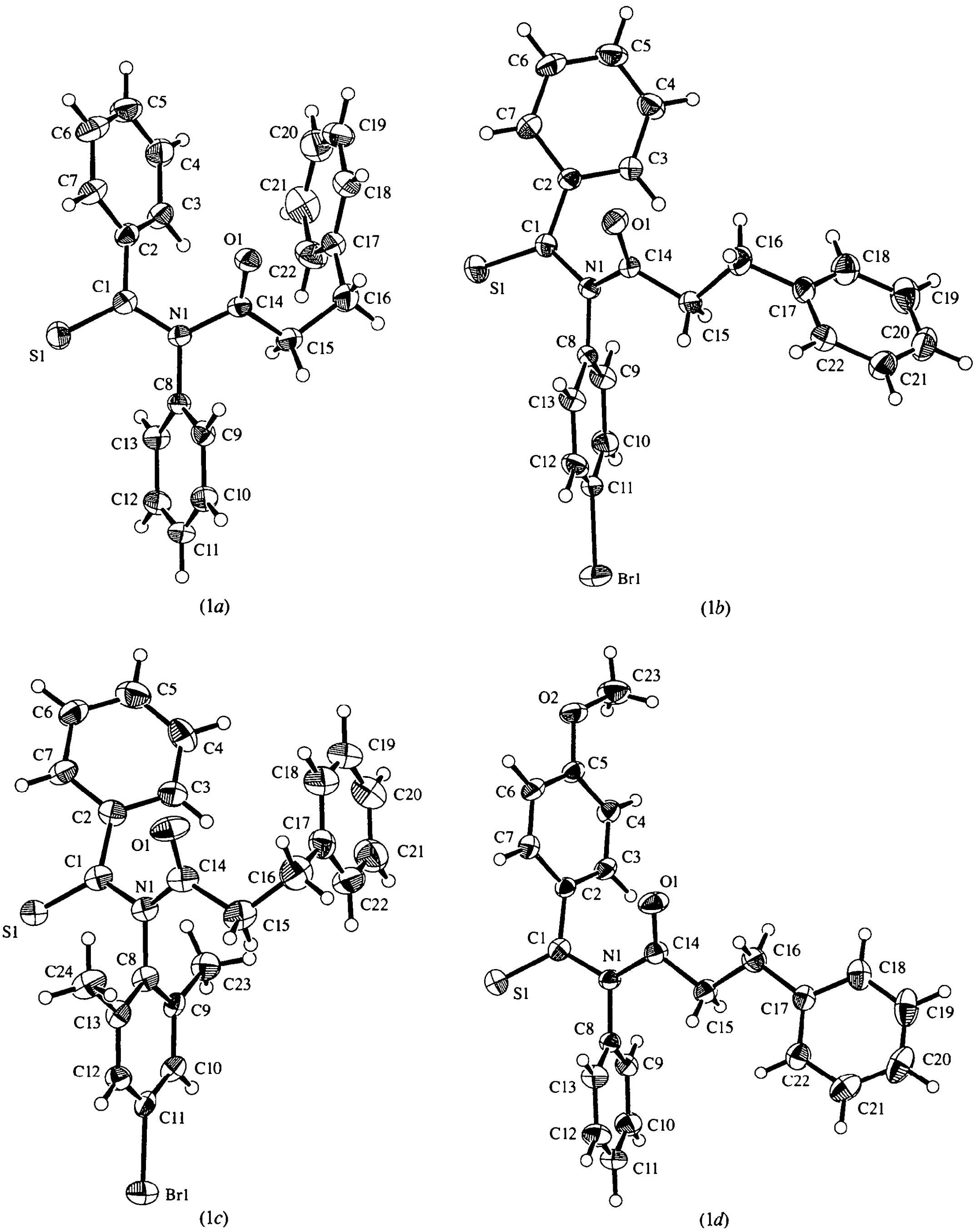
+

$Ph(CH_2)_2CO_2H$

As part of a determination of the geometrical requirements for intramolecular hydrogen abstraction by sulfur (Fu, Scheffer & Trotter, 1997), the monothioimides (1*a*)–(1*d*) have now been synthesized, their photochemistry studied [in solution and in the solid state; the solution photochemistry of (1*a*) and (1*d*) had been studied previously by Sakamoto *et al.* (1991)] and crystal structures determined. Irradiation with a 450 W Hanovia lamp of solutions of (1*a*)–(1*d*) in anhydrous benzene results in no photochemical reaction (Fu, Scheffer & Trotter, 1994). In benzene which has been allowed to equilibrate with atmospheric moisture, photolysis gives the thiobenzanilides (2*a*)–(2*d*) and 3-phenylpropanoic acid. Irradiations in benzene containing 10% methanol give (2*a*)–(2*d*) and methyl 3-phenylpropanoate. Photolysis of (1*a*)–(1*d*) in the solid state with rigorous exclusion of moisture again results in no photoreaction; when no special attempts are made to exclude moisture, irradiation leads to the same two photoproducts that are formed in benzene solution.

The crystal structure determinations of the monothioimides (1*a*)–(1*d*) show that all four molecules adopt similar (E_S,Z_O) conformations in the solid state (Fig. 1). *MMX* calculations (*PCModel*; Serena Software, 1988) indicate that this is the most stable conformation, presumably as a result of more favourable alignment of the carbonyl and thiocarbonyl dipoles, and smaller 1,3-steric repulsions (Fu, 1994). The (E_O,Z_S) conformation (scheme above), which is required for γ-hydrogen abstraction by sulfur, is higher in energy by 1.5 kJ mol^{-1}, with the (*Z,Z*) and (*E,E*) conformations intermediate in energy [1 kJ mol^{-1} above (E_S,Z_O)]. In the observed (E_S,Z_O) conformation, the shortest C═S···γ-H contacts [S1···H(on C15); Fig. 1] are 5.06, 5.14, 5.07 and 5.07 Å, for (1*a*)–(1*d*), respectively, considerably greater than the sum of the van der Waals radii for S and H (3.00 Å), and too distant to allow for hydrogen abstraction (Fu *et al.*, 1997). The shortest S···δ-H contacts are even longer (6.2–6.6 Å). To verify the lack of hydrogen abstraction, monothioimide (1*a*) containing two γ-deuterium atoms was synthesized and subjected to benzene-solution and solid-state photolysis under non-anhydrous conditions. In each case, the 3-phenylpropanoic acid photoproduct shows no loss of the deuterium label (γ-hydrogen abstraction would lead to a monodeuterated acid). Further corroboration is obtained by irradiating unlabelled (1*a*) in CH_3OD/benzene, which gives undeuterated methyl 3-phenylpropionate.

Hence it is established that photocleavage of monothioimides does not involve initial γ-hydrogen abstraction by sulfur, and another mechanism must be sought. A clue to a reasonable mechanistic possibility is found in the observed intramolecular contacts between the O atoms of the carbonyl (CO) groups and the C atoms of the thiocarbonyl (CS) groups: O1···C1 = 2.862 (3),



(1*a*) (1*b*) (1*c*) (1*d*)

Fig. 1. Views of the molecules of (1*a*), (1*b*), (1*c*) and (1*d*) (33% probability ellipsoids).

2.769 (3), 2.807 (7) and 2.811 (3) Å, for (1*a*)–(1*d*), respectively (Fig. 1). These distances are well below the sum of the van der Waals radii for O and C (3.22 Å), so that the O atom is ideally positioned for excited-state nucleophilic attack on the C=S double bond. A mechanism may therefore be proposed (Fig. 2) involving formation of a 1,3-oxazetidinium ion, (3), which could react with water present in the reaction medium to form (4), which could then break down, by a process which has been observed previously (Barton *et al.*, 1973), to form the enol of the thiobenzanilide and 3-phenylpropanoic acid. Attempts to trap the intermediate (3) with methyl iodide were unsuccessful.

Having established that photocleavage of the monothioimides (1*a*)–(1*d*) does not involve γ-hydrogen abstraction, it was of interest to discover whether fully oxygenated imides behave similarly. To this end, *N*-acetylpropanamide was synthesized and photolysed in CH_3OD; incorporation of one deuterium atom into the methyl propanoate photoproduct indicates that γ-hydrogen abstraction is occurring in this case (Mazzocchi *et al.*, 1980). This is in accord with the preferred (*E,Z*) conformation for such imides in solution (Noe & Raban, 1975), which has the abstracting O and abstracted H in close proximity.

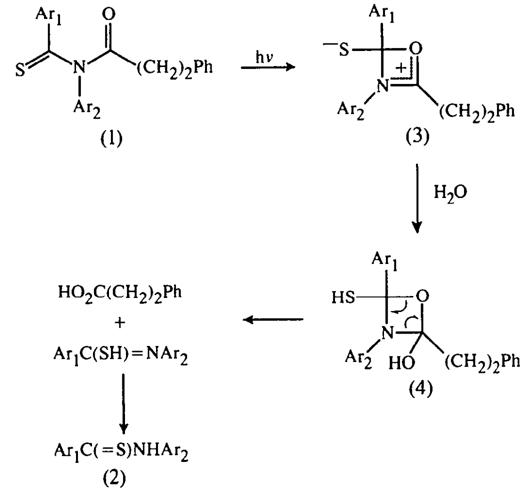


Fig. 2. Proposed mechanism for the photoreaction of the monothioimides.

All four monothioimide molecules, (1*a*)–(1*d*), have normal geometry and dimensions. The thioimide groups are roughly planar, presumably as a result of delocalization of the N-atom lone-pair electrons into the carbonyl and thiocarbonyl π systems. The S=C—N—CO grouping deviates from an exact *anti* (*E*) conformation by 20–30° [torsion angles −158.3 (2), −145.7 (2), −146.8 (4) and −149.2 (2)°; Table 1], and the SC—N—C=O grouping deviates by up to 30° from an exact *syn* (*Z*) conformation [torsion angles 29.9 (3), 23.8 (4), 13.4 (8) and 0.4 (4)°]. The phenylpropyl chains have *anti* conformations in (1*b*) and (1*d*) [C14—C15—C16—C17 torsion angles −167.6 (3) and 178.0 (2)°, respectively], but *gauche* conformations in (1*a*) and (1*c*) [torsion angles −68.6 (3) and −68.4 (7)°, respectively].

Experimental

Details of the synthesis and photochemistry have been deposited with the IUCr.

Compound (1*a*)

Crystal data

$C_{22}H_{19}NOS$
$M_r = 345.46$
Orthorhombic
$P2_12_12_1$
$a = 8.022\,(4)$ Å
$b = 38.685\,(4)$ Å
$c = 5.847\,(3)$ Å
$V = 1815\,(1)$ Å^3
$Z = 4$
$D_x = 1.264$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 24 reflections
$\theta = 44.3$–$54.3°$
$\mu = 1.598$ mm^{-1}
$T = 294$ K
Prism
0.30 × 0.15 × 0.15 mm
Orange

Data collection

Rigaku AFC-6*S* diffractometer
ω–2θ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.633$, $T_{max} = 0.787$
2113 measured reflections
2113 independent reflections

1861 reflections with $I > 3\sigma(I)$
$\theta_{max} = 77.42°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 48$
$l = 0 \rightarrow 6$
3 standard reflections every 200 reflections intensity decay: 0.17%

Refinement

Refinement on F^2
$R(F) = 0.030$
$wR(F^2) = 0.085$ (0.113 for the enantiomeric structure)
$S = 1.71$
2113 reflections
227 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + 0.00022(F_o^2)^2]$

$(\Delta/\sigma)_{max} = 0.019$
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}
Extinction correction: Zachariasen (1967)
Extinction coefficient: $4.3\,(7) \times 10^{-6}$
Scattering factors from *International Tables for Crystallography* (Vol. C)

Compound (1*b*)

Crystal data

$C_{22}H_{18}BrNOS$
$M_r = 424.35$
Monoclinic
$P2_1/a$
$a = 9.506\,(1)$ Å
$b = 17.643\,(2)$ Å
$c = 11.960\,(1)$ Å
$\beta = 91.65\,(1)°$
$V = 2005.1\,(4)$ Å^3
$Z = 4$
$D_x = 1.406$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 23 reflections
$\theta = 55.6$–$57.0°$
$\mu = 3.839$ mm^{-1}
$T = 294$ K
Prism
0.60 × 0.40 × 0.30 mm
Orange

Data collection

Rigaku AFC-6*S* diffractometer
ω–2θ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.171$, $T_{max} = 0.316$
4584 measured reflections
4178 independent reflections

3479 reflections with $I > 3\sigma(I)$
$R_{int} = 0.015$
$\theta_{max} = 77.47°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 22$
$l = -15 \rightarrow 15$
3 standard reflections every 200 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.044$
$wR(F^2) = 0.130$
$S = 3.63$
4178 reflections
236 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + 0.00006(F_o^2)^2]$
$(\Delta/\sigma)_{\max} = 0.007$
$\Delta\rho_{\max} = 0.83$ e Å^{-3} (0.9 Å from Br)
$\Delta\rho_{\min} = -0.70$ e Å^{-3}
Extinction correction: Zachariasen (1967)
Extinction coefficient: $8.6 (4) \times 10^{-6}$
Scattering factors from *International Tables for Crystallography* (Vol. C)

Compound (1*c*)

Crystal data

$C_{24}H_{22}BrNOS$
$M_r = 452.41$
Orthorhombic
$Pca2_1$
$a = 38.032 (3)$ Å
$b = 7.373 (4)$ Å
$c = 7.725 (4)$ Å
$V = 2166 (2)$ Å^3
$Z = 4$
$D_x = 1.387$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 12.6–16.3°$
$\mu = 1.983$ mm^{-1}
$T = 294$ K
Prism
0.30 × 0.20 × 0.20 mm
Red

Data collection

Rigaku AFC-6*S* diffractometer
ω scan
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.650$, $T_{\max} = 0.673$
2844 measured reflections
2844 independent reflections
1302 reflections with $I > 3\sigma(I)$
$\theta_{\max} = 30.00°$
$h = 0 \rightarrow 53$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 10$
3 standard reflections every 200 reflections intensity decay: 3.3%

Refinement

Refinement on F^2
$R(F) = 0.033$
$wR(F^2) = 0.082$ (0.100 for opposite polarity)
$S = 1.18$
2844 reflections
252 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + 0.00016(F_o^2)^2]$
$(\Delta/\sigma)_{\max} = 0.004$
$\Delta\rho_{\max} = 0.87$ e Å^{-3}
$\Delta\rho_{\min} = -2.16$ e Å^{-3} (at Br site)
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Compound (1*d*)

Crystal data

$C_{23}H_{21}NO_2S$
$M_r = 375.48$
Orthorhombic
Pbca
$a = 26.345 (6)$ Å
$b = 24.531 (7)$ Å
$c = 6.073 (10)$ Å
$V = 3925 (9)$ Å^3
$Z = 8$
$D_x = 1.271$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 17 reflections
$\theta = 10.1–18.9°$
$\mu = 0.182$ mm^{-1}
$T = 294$ K
Prism
0.30 × 0.30 × 0.15 mm
Orange–red

Data collection

Rigaku AFC-6*S* diffractometer
$\omega–2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.904$, $T_{\max} = 1.000$
5741 measured reflections
5741 independent reflections
1604 reflections with $I > 3\sigma(I)$
$\theta_{\max} = 30.01°$
$h = 0 \rightarrow 37$
$k = 0 \rightarrow 34$
$l = -8 \rightarrow 0$
3 standard reflections every 200 reflections intensity decay: 1.0%

Refinement

Refinement on F^2
$R(F) = 0.046$
$wR(F^2) = 0.122$
$S = 1.03$
5741 reflections
244 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + 0.00022(F_o^2)^2]$
$(\Delta/\sigma)_{\max} = 0.0013$
$\Delta\rho_{\max} = 0.87$ e Å^{-3} (0.6 Å from S)
$\Delta\rho_{\min} = -1.07$ e Å^{-3} (at S site)
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Comparison of selected bond distances (Å) and angles (°)*

	(1*a*)	(1*b*)	(1*c*)	(1*d*)
C—Br		1.897 (2)	1.907 (5)	
C1═S1	1.643 (2)	1.630 (2)	1.632 (6)	1.628 (2)
C14═O1	1.202 (3)	1.204 (3)	1.194 (6)	1.202 (2)
N1—C1	1.383 (2)	1.398 (3)	1.399 (7)	1.397 (3)
N1—C14	1.431 (2)	1.417 (3)	1.418 (7)	1.433 (3)
C1—N1—C8	120.3 (2)	121.1 (2)	117.5 (4)	118.2 (2)
C1—N1—C14	123.0 (2)	120.2 (2)	122.4 (4)	122.5 (2)
C8—N1—C14	115.8 (2)	118.1 (2)	119.1 (5)	118.2 (2)
S1═C1—N1—C14	−158.3 (2)	−145.7 (2)	−146.8 (4)	−149.2 (2)
C1—N1—C14═O1	29.9 (3)	23.8 (4)	13.4 (8)	0.4 (4)

H atoms were fixed in ideal sites; for (1*c*), the methyl H-atom sites were based on difference peaks.

For all compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1995); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1342). Services for accessing these data are described at the back of the journal. Details of the synthesis and photochemistry of the four title compounds have also been deposited.

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Bis(4-butoxyphenyl) Terephthalate

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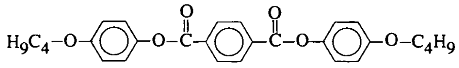
Abstract

The crystal and molecular structures of nematogenic bis(4-butoxyphenyl) terephthalate, $C_{28}H_{30}O_6$, are reported. The molecular structure, determined by X-ray diffraction, is very different from that of the same compound reported on the basis of solid-state NMR analysis [Uryu & Kato (1988). *Macromolecules*, **21**, 378–384]. In the structure reported here, the carbonyl group of the ester is, as expected, almost coplanar with the phenyl ring of the terephthalate. The conformation of the aliphatic chain is not fully *trans*-planar; there is a *gauche* bond. Molecules are stacked in layers with a herring-bone type of packing within the layers.

Comment

Terephthalic and *p*-hydroxybenzoic acids are among the most widely used groups for the synthesis of both monomers and polymers which form liquid crystals. Condensation of these groups with various *p,p'*-difunctionalized aromatic compounds leads to linear high axial ratio structures (esters, amides, *etc.*) which favor the formation of liquid-crystal phases (Ober, Jin & Lenz, 1984). In previously reported structures of esters of terephthalic, *p*-hydroxybenzoic and related aromatic carboxylic acids (Schweizer & Dunitz, 1982; Centore *et al.*, 1991), the carbonyl group of the ester is found to be coplanar or almost coplanar with the phenyl ring to which it is attached. Consistent with this, semi-empirical quantum-mechanical calculations for 'gas-phase' phenyl benzoate (Bicerano & Clark, 1988) indicate an energy about 6.7 kcal mol^{-1} greater for the 'perpendicular' arrangement of carbonyl group and phenyl ring, compared with the lowest energy coplanar conformation. Deviations from the coplanar arrangement are only observed as a result of great overcrowding, *e.g.* in the crystal structures of 2,6-disubstituted benzoic acids (Anca, Martinez-Carrera & Garcia-Blanco, 1967; Florencio & Smith, 1970). On the basis of solid-state CP/MAS NMR analysis on crystals of the title compound, (I), Uryu & Kato (1988) reported that the carbonyl group of the ester is almost perpendicular to the plane of the terephthalate phenyl ring. They also reported that the planes of the three phenyl rings of the molecule were parallel, which is rare in the crystal structures of phenyl esters of aromatic acids, and that the aliphatic chains were planar zigzag. We undertook the crystal structure determination reported here in order to establish definitively the conformation in the solid state.



(I)

The thermal properties of the title compound as prepared by us are consistent with literature data (crystal–nematic transition: T_m = 460.4 K, ΔH_m = 45.8 kJ mol^{-1}; nematic–isotropic transition: T_i = 505.0 K, ΔH_i = 0.45 kJ mol^{-1}). Particular care was taken to detect possible solid-state polymorphs; samples recrystallized from ethyl acetate [as reported by Uryu & Kato (1988)] and from various other solvents or solvent mixtures (chloroform–ethanol, chloroform–*n*-hexane, toluene) all have identical DSC thermograms.

The molecules in the crystals are centrosymmetric and belong to point group $\bar{1}$ (C_i). Bond lengths and angles have normal values. The conformation of the molecule, however, is considerably different from that proposed by Uryu & Kato (1988). The carbonyl group of the ester is almost coplanar with the phenyl ring of the terephthalate [O3—C11—C12—C13 −176.3 (2)°], as is usual in terephthalate esters. The dihedral angle between the planes of the two phenyl rings, C5–C10 and C12–C14, is 65.06 (5)° and is mainly due to the torsion angle around the O2—C8 bond. Furthermore, the conformation of the aliphatic chain is not fully *trans*-planar, a *gauche* conformation being observed around the C3—C4 bond.

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